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Correlation matrix renormalization theory for correlated-electron materials with application to the crystalline phases of atomic hydrogen

Xin Zhao
Ames Laboratory, xzhao@iastate.edu

Jun Liu
Ames Laboratory

Cai-Zhuang Wang
Ames Laboratory, wangcz@ameslab.gov

Kai-Ming Ho
Iowa State University and Ames Laboratory, kmh@iastate.edu

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Correlation matrix renormalization theory for correlated-electron materials with application to the crystalline phases of atomic hydrogen

Abstract
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Correlation matrix renormalization theory for correlated-electron materials with application to the crystalline phases of atomic hydrogen

Xin Zhao, Jun Liu,* Yong-Xin Yao, Cai-Zhuang Wang, and Kai-Ming Ho
Ames Laboratory, U.S. DOE and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

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Developing accurate and computationally efficient methods to calculate the electronic structure and total energy of correlated-electron materials has been a very challenging task in condensed matter physics and materials science. Recently, we have developed a correlation matrix renormalization (CMR) method which does not assume any empirical Coulomb interaction U parameters and does not have double counting problems in the ground-state total energy calculation. The CMR method has been demonstrated to be accurate in describing both the bonding and bond breaking behaviors of molecules. In this study, we extend the CMR method to the treatment of electron correlations in periodic solid systems. Using a linear hydrogen chain as a benchmark system, we show that the results from the CMR method compare very well with those obtained recently by accurate quantum Monte Carlo (QMC) calculations. We also study the equation of states of three-dimensional crystalline phases of atomic hydrogen. We show that the results from the CMR method agree much better with the available QMC data in comparison with those from density functional theory and Hartree-Fock calculations.

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I. INTRODUCTION

In the past several decades, great efforts have been devoted to the development of robust and efficient theoretical and computational methods to accurately treat materials containing strongly correlated electrons. Although the theoretical framework has been established, namely, the many-body Schrödinger equation [1], the combinatorial growth of the computational cost in solving such an interacting-electron equation brings great challenges to the physics and chemistry communities. No method presently exists that can treat many-electron bulk materials exactly at low computational cost. Accurate methods available from quantum chemistry approaches (e.g., configuration interaction) and quantum Monte Carlo (QMC) simulation restrict the size of systems that can be handled, and are too expensive to perform the calculations for condensed matter systems. While density functional theory (DFT) is highly effective and has been successful in predicting the physical properties of many materials, they fail for systems with strongly correlated electrons.

In the past two decades, there has been considerable progress in new theories, algorithms, and computational methods to address interacting electrons in the condensed matter systems. Among these new developments, hybrid approaches which merge DFT with many-body methods, such as local-density approximation plus on-site Coulomb interaction (LDA + U) [2,3], LDA + dynamical mean-field theory (LDA + DMFT) [4–6], and LDA + Gutzwiller (LDA + G) [7–12], have been demonstrated to be useful in describing real correlated materials. However, the use of adjustable screened Coulomb U and J parameters in these calculations limits the predictive power of the methods.

Recently, we have been developing a computationally efficient method for ground-state total energy calculations of correlated-electron systems, aiming at avoiding the use of adjustable U and J parameters [13–15]. Our approach, called the correlation matrix renormalization (CMR) approximation, extends the commonly adopted Gutzwiller approximation (GA) for evaluating the one-particle density matrix [16–19] to the two-particle correlation matrix of the system. The CMR method has no adjustable parameters and no double counting issues in the calculation of total energy. The computational workload of the CMR method scales as N^4 or better with respect to the system size N [similar to Hartree-Fock (HF)] and has been well benchmarked in several molecule systems [14,15]. Since our CMR theory uses some approximations to enable computational efficiency, further benchmark tests of the accuracy of the method for more complex systems are necessary.

In this paper, we extend the CMR method to treat electron corrections in periodic bulk solids. We demonstrate the accuracy of the method by comparing the results from the CMR calculations with those from accurate quantum Monte Carlo (QMC) calculations available in the literature [20,21] for crystalline phases of atomic hydrogen. We show that results from the CMR method agree well with very recent accurate QMC calculations on a one-dimensional (1D) linear chain of atomic hydrogen [20]. We have also calculated the total energy and pressure-volume phase diagram at zero temperature for three-dimensional (3D) atomic H lattices, including the simple cubic (sc), body-centered cubic (bcc), face-centered cubic (fcc), and diamond (dia) phases. The results from the CMR calculations are also in good agreement with the limited available data from QMC calculations [21]. Our calculations provide useful insights into the phase evolutions of atomic H crystal structures under pressure.

*Present address: Department of Physics, University of Virginia, Charlottesville, VA 22904.

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II. CMR METHOD

The Hamiltonian for an interacting many-electron system in the second quantization form can be expressed as

$$H_{\rm CMR} = \sum_{Ii\Gamma} E_{Ii\Gamma}|\Gamma_{Ii}\rangle\langle\Gamma_{Ii}| + \sum_{Ii\alpha,Jj\beta,\sigma}{}' t_{Ii\alpha Jj\beta} c^{\dagger}_{Ii\alpha\sigma} c_{Jj\beta\sigma} + \frac{1}{2}\sum_{\substack{Ii\alpha,Jj\beta,\\ Kk\gamma,Ll\delta,\sigma\sigma'}}{}' U^{Kk\gamma,Ll\delta}_{Ii\alpha,Jj\beta} c^{\dagger}_{Ii\alpha\sigma} c^{\dagger}_{Jj\beta\sigma'} c_{Ll\delta\sigma'} c_{Kk\gamma\sigma}, \tag{1}$$

where I, J, K, L represent the unit cell indices; i, j, k, l are atomic site indices; $\alpha, \beta, \gamma, \delta$ are orbital indices; σ, σ' are spin indices, respectively. $c^{\dagger}_{Ii\alpha\sigma}$ and $c_{Jj\beta\sigma}$ are electron creation and annihilation operators. The primed sum, Σ', means that the pure local on-site terms are excluded from the summation. The first term is the local on-site Hamiltonian which can be treated exactly with $E_{Ii\Gamma}$ being the energy of a local many-body configuration $|\Gamma_{Ii}\rangle$. The second term describes the nonlocal one-body contribution with t being the one-electron hopping integral which is expressed as [22]

$$t_{Ii\alpha Jj\beta} = \langle\phi_{Ii\alpha}|\hat{T} + \hat{V}_{\rm ion}|\phi_{Jj\beta}\rangle, \tag{2}$$

where $\hat{T}$ and $\hat{V}_{\rm ion}$ are the operators for kinetic energy and electron-ion interaction of a single electron. In the nonlocal two-body contribution term, U is the two-electron Coulomb integral expressed as

$$U^{Kk\gamma,Ll\delta}_{Ii\alpha,Jj\beta} = \iint \phi^{*}_{i\alpha}(\boldsymbol{r}-\boldsymbol{R_I})\phi^{*}_{k\gamma}(\boldsymbol{r}-\boldsymbol{R_K})U(\boldsymbol{r}-\boldsymbol{r'})\phi_{j\beta}(\boldsymbol{r'}-\boldsymbol{R_J})\phi_{l\delta}(\boldsymbol{r'}-\boldsymbol{R_L})drdr'. \tag{3}$$

All interactions are included in this Hamiltonian without any adjustable parameters. In the CMR approach, we evaluate Eq. (1) with the Gutzwiller variational wave functions (GWFs) constructed from a noninteracting wave function $|\Psi_0\rangle$,

$$|\Psi_{\rm G}\rangle = \prod_{Ii}\left(\sum_{\Gamma} g_{Ii\Gamma}|\Gamma_{Ii}\rangle\langle\Gamma_{Ii}|\right)|\Psi_0\rangle. \tag{4}$$

Here, $g_{Ii\Gamma}$ are the Gutzwiller variational parameters which are used to optimize the occupation probabilities $p_{Ii\Gamma}$ of the local configurations $|\Gamma_{Ii}\rangle$. Assuming the Wick's theorem holds approximately, the total energy of the system within the CMR theory can be expressed as [13–15]

$$\begin{aligned} E_{\rm CMR} = &\sum_{Ii\Gamma} E_{Ii\Gamma} p_{Ii\Gamma} + \sum_{Ii\alpha,Jj\beta,\sigma}{}' t_{Ii\alpha Jj\beta}\langle c^{\dagger}_{Ii\alpha\sigma} c_{Jj\beta\sigma}\rangle_G \\ &+ \frac{1}{2}\sum_{\substack{Ii\alpha,Jj\beta,\\ Kk\gamma,Ll\delta,\sigma\sigma'}}{}' U^{Kk\gamma,Ll\delta}_{Ii\alpha,Jj\beta}(\langle c^{\dagger}_{Ii\alpha\sigma} c_{Kk\gamma\sigma}\rangle_G\langle c^{\dagger}_{Jj\beta\sigma'} c_{Ll\delta\sigma'}\rangle_G - \delta_{\sigma\sigma'}\langle c^{\dagger}_{Ii\alpha\sigma} c_{Ll\delta\sigma}\rangle_G\langle c^{\dagger}_{Jj\beta\sigma} c_{Kk\gamma\sigma}\rangle_G) + E_c. \end{aligned} \tag{5}$$

Following the idea of the well-established Gutzwiller approximation (GA) [18,19], $\langle c^{\dagger}_{Ii\alpha\sigma} c_{Jj\beta\sigma}\rangle_G \equiv \langle\Psi_{\rm G}|c^{\dagger}_{Ii\alpha\sigma} c_{Jj\beta\sigma}|\Psi_{\rm G}\rangle$ is evaluated as

$$\langle c^{\dagger}_{Ii\alpha\sigma} c_{Jj\beta\sigma}\rangle_G = z^{Jj\beta}_{Ii\alpha,\sigma}\langle c^{\dagger}_{Ii\alpha\sigma} c_{Jj\beta\sigma}\rangle_0,$$

where $z^{Jj\beta}_{Ii\alpha,\sigma}$ is introduced following the spirit of GA and can be evaluated as $z^{Jj\beta}_{Ii\alpha,\sigma} = z_{Ii\alpha\sigma} z_{Jj\beta\sigma}$ if $(Ii\alpha) \neq (Jj\beta)$ and 1 otherwise. $z_{Ii\alpha\sigma}$ is known as the one-electron renormalization factor, and in the cases where Coulomb and exchange integrals are dominant in the on-site Hamiltonian, it can take the following form:

$$z^{\rm GA}_{Ii\alpha\sigma} = \sum_{\Gamma\Gamma'}\sqrt{p_{Ii\Gamma}p_{Ii\Gamma'}}\langle\Gamma|c^{\dagger}_{Ii\alpha\sigma}|\Gamma'\rangle\Big/\sqrt{n^0_{Ii\alpha\sigma}\left(1-n^0_{Ii\alpha\sigma}\right)}, \tag{6}$$

with $n^0_{Ii\alpha\sigma} = \langle c^{\dagger}_{Ii\alpha\sigma} c_{Ii\alpha\sigma}\rangle_0 \equiv \langle\Psi_0|c^{\dagger}_{Ii\alpha\sigma} c_{Ii\alpha\sigma}|\Psi_0\rangle$.

In the CMR theory, the best form of the z factors in finite dimensions is not necessarily the same as the one from the standard GA shown in Eq. (6), which is only exact in the infinite dimension. Meanwhile, the factorization of the intersite two-body interactions into renormalized Hartree and exchange terms according to Wick's theorem also introduces errors for the expectation value with respect to GWF. The last term E_c in Eq. (5) accounts for the residual correlation energy due to the approximations used in our CMR theory.

We found that the residual correlation energy E_c can be substantially reduced by replacing the expression for the one-electron renormalization factor z from the GA of Eq. (6) with a more optimal formula. In our earlier works [14], the z is replaced by a functional $f(z)$, which is optimized by fitting to the results of some exactly solved reference systems. More recently, by comparing the total energy expression from our CMR theory with the exact solution for the H_2 molecule under a minimal basis set, we showed that the one-electron renormalization factor z is better expressed as the square root of the results from Eq. (6); i.e., the z factor in CMR should be equal to $\sqrt{z_{\rm GA}}$ [15]. At the same time, a sum-rule correction term can be added to Eq. (1) to minimize the error in the evaluation of the intersite Coulomb integral using Wick's theorem [15]. In the H_2 case, the sum-rule correction

term is

$$H_{\text{sum-rule}} = \frac{1}{2}\sum_{Ii\alpha\sigma}\lambda_{Ii\alpha\sigma}\hat{n}_{Ii\alpha\sigma}\left(\sum_{Jj\beta\sigma'}\hat{n}_{Jj\beta\sigma'} - N_e\right), \tag{7}$$

where $\lambda_{Ii\alpha\sigma}$ is the weighting factor. In this study of solid systems, we employ the general form of $\lambda_{Ii\alpha\sigma}$ derived in the supporting information of Ref. [15],

$$\lambda_{Ii\alpha\sigma} = -\frac{\sum_{Jj\neq Ii}\sum_{\beta,\sigma}U^{Ii\alpha,Jj\beta}_{Ii\alpha,Jj\beta}|\langle c^{\dagger}_{Ii\alpha\sigma}c_{Jj\beta\sigma}\rangle_{\text{CMR}}|^4}{\sum_{Jj\neq Ii}\sum_{\beta,\sigma}|\langle c^{\dagger}_{Ii\alpha\sigma}c_{Jj\beta\sigma}\rangle_{\text{CMR}}|^4}. \tag{8}$$

It has been demonstrated [15] that in the CMR approach, the sum rule provides a natural way to improve the accuracy by shifting the nonlocal intersite terms to local on-site terms. Its exact form is not crucial as long as it decays sufficiently fast.

Finally, after the local corrections discussed above, the residual correlation energy E_c in our CMR calculations for solid-state systems will be treated in a mean-field manner. In the present study, E_c in the E_{CMR} of Eq. (5) is evaluated using the local density approximation under DFT. The total energy in the solid systems is written as

$$E = E_{\text{CMR}} + E_{\text{sum-rule}}. \tag{9}$$

We note that by including the correlation energy from LDA, the atom energy from the CMR calculation will be changed accordingly. This can be fixed by performing a constant shift so that the CMR energy at large separation is consistent with or without considering E_c (LDA).

The CMR method has been implemented through an interface with VASP [23]. The quasiatomic minimal basis-set orbitals (QUAMBOs) we developed earlier are utilized as the local basis set to represent the Hamiltonian [24,25]. The connection to VASP is straightforward since QUAMBOs are expressed in terms of plane waves. The detailed implementations will be presented in a follow-up publication. In principle, the local basis orbitals implemented in the CMR can be variationally optimized to further improve the accuracy of the calculations [26]. We performed such optimization for the H_2 molecule starting from the QUAMBOs and found the effects of the optimization are very small due to the fact that in our scheme of constructing the QUAMBOs, the effects of the bonding environment on the size and shape of the local basis orbitals have been taken into account [24]. In the present study of crystalline structures of atomic hydrogen, different QUAMBOs are constructed for different types of crystal structures and at different lattice constants. Therefore, the environment dependence of the local basis orbital is included in our calculations.

III. RESULTS AND DISCUSSIONS

As the most abundant element in nature, structures and physical properties of possible crystalline phases of atomic hydrogen have attracted continuous scientific interest over centuries. Despite the simplicity of the hydrogen atom, its bulk phases have been shown to display amazingly rich behaviors [27–32]; especially, the search for superconducting metallic hydrogen phases continuously attracts a great deal of attention [33–36]. Theoretical calculations based on crystal structure prediction and DFT energy evaluation methods have been playing an important role in the study of solid H phases [28,29,31]. However, the accuracy of current DFT calculations in describing the structures, stabilities, and properties of the crystalline phases of atomic hydrogen has been under intense debate [31]. Bulk phases of atomic hydrogen are also the test ground for the development of theories and computational methods for correlated-electron materials [20].

A. One-dimensional chain of atomic hydrogen

We first benchmark the accuracy of our CMR method by comparing the results of the energy of a 1D hydrogen chain as a function of interatomic distance from our CMR calculations with those available in the literature using other methods. The linear H chain is the simplest periodic system made of real matter, yet it serves as an important test ground for the development of many-body methods to treat correlation effects in real materials. On one hand, as the H-H distance is increased, electron correlations can span over a wide range of strengths. Thus the full physical Coulomb interaction needs to be treated for accurate description of this system. On the other hand, the H chain avoids the complexities of treating core electrons and incorporating relativistic effects. Therefore, the H chain is accessible to many theoretical methods at their current state of development, as discussed in detail in one of the recent reports [20]. Results obtained from more than a dozen many-body computational methods were presented in Ref. [20], and can serve as a useful dataset for our benchmarking purposes.

In Fig. 1, we compare the equation of state of the 1D H chain calculated using our CMR approach with the data calculated

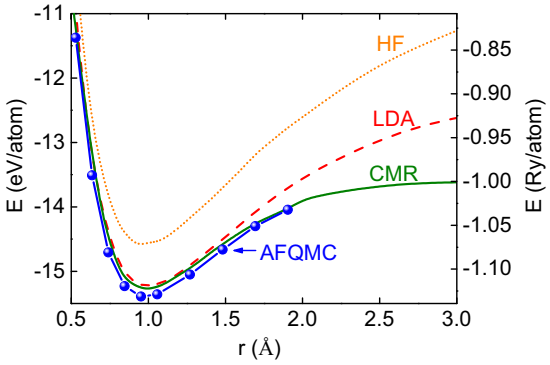

FIG. 1. Equation of state of the one-dimensional hydrogen chain calculated from different methods as indicated.

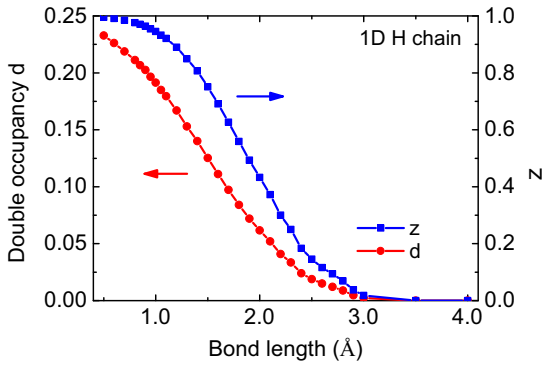

FIG. 2. Double occupancy weight d and the one-electron renormalization factor z of 1D hydrogen chain as a function of bond length calculated from the CMR method.

using auxiliary-field quantum Monte Carlo (AFQMC) reported in Ref. [20]. The results from density functional calculations with local density approximation (LDA) and the Hartree Fock (HF) method are also plotted for comparison.

From Fig. 1, it can be seen that the accuracy of CMR nearly reaches the level of AFQMC and performs better than the standard LDA, especially when the atomic separation gets larger. Although our CMR method is based on HF calculations, it provides a much better description of the 1D hydrogen system than HF. In addition, we also note that the CMR method provides the correct atomic limit (–13.6 eV) as the bond separation is large enough, while all the other methods fail except QMC, as one can see in more detail in Ref. [20].

In Fig. 2, we plotted the local on-site double occupancy weight and z factor of the 1D H chain calculated from CMR. As the bond length increases, the double occupancy is gradually suppressed, similar to the previously calculated hydrogen clusters H_n [14,15]. In the cases of H_n molecules, large errors in HF and LDA have been attributed to their constant double occupancy, which contributes an energy term in proportion to the on-site Coulomb integral. Likewise, the error in HF and LDA in the 1D H chain can also be explained by the incorrect double occupancy.

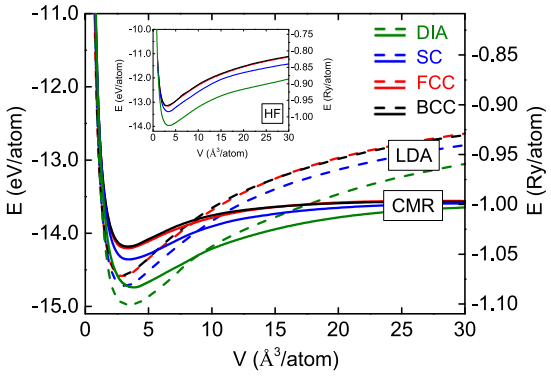

FIG. 3. Equation of state calculated for the 3D hydrogen lattices from LDA (dashed lines) and CMR (solid lines). Different lattices are distinguished by color. The HF results are plotted in dotted lines and shown in the inset.

TABLE I. Equilibrium volume (V_0) and bulk modulus (B) of the 3D H lattices fitted using the Murnaghan equation of state.

	V_0(Å^3/atom)		B (GPa)	
Structure	LDA	CMR	LDA	CMR
dia	3.28	3.59	118.8	98.2
sc	3.07	3.30	117.2	109.1
fcc	2.93	3.20	135.2	109.8
bcc	2.94	3.32	116.3	86.2

Previous variational Monte Carlo studies have suggested that, at the crossover between the weakly (small bond length) and strongly (large bond length) correlated regimes, the hydrogen chain goes through a metal to insulator phase transition based on the variation of the electronic polarization [37]. Yet from our calculation, we note that the change in the double occupancy and the renormalization factor z is rather smooth; hence the metal to insulator transition appears to be a crossover based on our CMR calculation. It has been shown that the Mott physics such as the intersite spin correlations and incoherent double excitations may not be well described by the Gutzwiller approximation (GA) [38–40]. The lack of sharp Mott transition in the 1D hydrogen chain shown in Fig. 2 would be partially attributed to the use of GA in our CMR theory. Nevertheless, we also would like to note that although our CMR theory inherits the physically most meaningful concept of renormalized hopping from the GA, it contains a much better treatment of the intersite Coulomb interactions, particularly through the two-electron density matrix sum-rule corrections.

B. Three-dimensional hydrogen lattices

Next we apply the CMR calculations to 3D lattices of atomic hydrogen. Crystal structures of hydrogen under pressure have been intensively studied but the details of the phase transition under pressure are still under debate. Here only the simplest lattices of hydrogen, such as sc, bcc, fcc, and dia under pressure

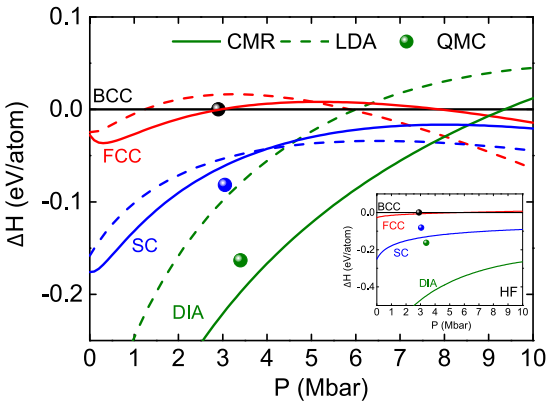

FIG. 4. The enthalpy of atomic hydrogen in different crystal structures relative to that of bcc phase calculated from LDA (dash lines) and CMR (solid lines). Three data points obtained from QMC calculations [21] are shown by balls with their color representing different crystal structures and matching with the lines. The results from HF are plotted as the inset.

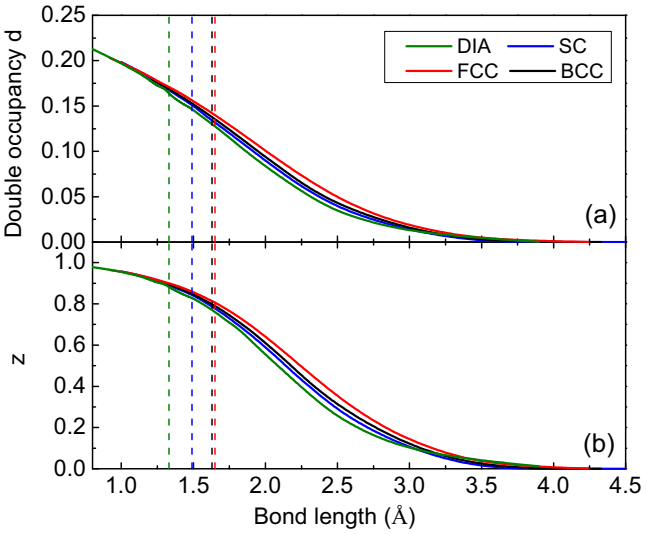

FIG. 5. (a) Double occupancy weight d and (b) the one-electron renormalization factor z of 3D atomic hydrogen lattices as a function of H-H bond length calculated from the CMR method. The dashed lines indicate the bond lengths corresponding to the equilibrium volumes.

are discussed to benchmark our CMR method because only a few quantum Monte Carlo data points are available in the literature for these simple structures at about 2–3 Mbar of pressure.

In Fig. 3, the results of energy as the function of volume from LDA, HF, and CMR are plotted. From the *E-V* data, we fitted the equilibrium volumes and bulk moduli of the four simple lattices of H and the results are listed in Table I. The CMR generally predicts a larger equilibrium volume than LDA which is known to consistently underestimate the lattice constants of solids. The bulk modulus predicted from CMR, on the other hand, is always smaller than that from LDA. It can also be noticed from Fig. 3 that the CMR method again provides the correct atomic limit as the volume of the unit cell is large enough, where both HF and LDA fail.

The enthalpy verses pressure curves calculated from the Murnaghan fitting are plotted in Fig. 4. The energetic order of phase stability is roughly the same among all the three calculations. Specifically, diamond structure has the lowest enthalpy in the smaller pressure range. As the pressure increases, sc becomes the most stable one, followed by the fcc structure. However, the transition pressures are quite different from different methods, as seen from the lowest line segments on the *P-H* curve. In the literature, limited data points calculated from QMC were found on the relevant phases [21], as shown by the ball points in Fig. 4. It can be seen from Fig. 4 that while the results from LDA and HF are very different from QMC results, the CMR results recover the QMC data points very well.

The calculated results of the double occupancy d and the one-electron renormalization factor z in the 3D atomic hydrogen lattice systems are plotted as Figs. 5(a) and 5(b), respectively. We can see that the variation of these properties as the function of bond length is similar to that in the 1D hydrogen chain. The calculation results also show that the electrons in the diamond lattice are more localized while those in the fcc lattice are more delocalized.

IV. CONCLUSIONS

In summary, we demonstrated that the CMR method is an accurate and efficient method for calculating the phase diagram of crystalline phases of atomic hydrogen at zero temperature. Differing from the LDA + U and LDA + DMFT types of methods, CMR is free of adjustable screened Coulomb interaction parameters and double counting issues in the calculation of strongly correlated-electron materials. The excellent agreement between the results of CMR calculation and that of accurate AFQMC on 1D atomic hydrogen chain is intriguing since many other methods fail to describe this system accurately [20]. In the cases of 3D atomic hydrogen lattices, the results from the CMR method also agree better with the QMC calculations than LDA and HF. Considering the computational cost of CMR being similar to HF and its performance on the hydrogen systems discussed in this work, we believe it is promising to extend its application to systems with more electrons and to address some of the long-standing issues in the strongly correlated materials.

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X.Z. and J.L. contributed equally to this work.

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